CHARACTERIZATION OF COAL PARTICLE SURFACES BY FILM FLOTATION

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ABSTRACT

Because of the heterogeneity of coal, particles may vary in composition and, consequently, each particle may have its own unique set of surface properties. The distribution of surface properties of coal particles was determined through film flotation with a series of aqueous methanol solutions. This paper shows how such measurements of the critical wetting surface tension can be used to determine the contact angle (θ) of particles and the distribution of lyophobic sites on the surface of the particles. The mean contact angles calculated from film flotation results for sulfur, graphite and a number of different coals are in reasonable agreement with the values reported in the literature.

INTRODUCTION

Characterization of coal particles in terms of their wetting properties is important for understanding the behavior of coal in such surface-based processes as flotation, agglomeration, filtration and dust abatement. The wetting properties of solids have commonly been studied by measuring contact angles on a flat surface (1) and determining the critical wetting surface tension from the well-known Zisman plot (2). This method has been very successful for assessing the wettability of homogeneous materials, such as polymers. However, because of the heterogeneity of coal, the results obtained using this approach by different researchers are inconsistent (3,4).

Because of the heterogeneity of coal, the properties of coal particles can range from those of a virtually pure inorganic mineral species to that of an organic material. Consequently, each particle may have its own unique set of surface characteristics. Standard measurements of liquid penetration rates, heat of immersion, immersion times, and freezing-front points can assess only average properties of particulate samples. Recently, a film flotation technique was developed wherein the fraction of particles that sink or float on liquids of different surface tensions can be determined (5,6), and from such determination the distribution of wetting surface tensions (surface energies) can be determined.

In this study, the distribution of the surface properties of coals was determined with 100 x 150 μm particles by film flotation on a series of aqueous methanol solutions (of different compositions). By separating the particles into the lyophobic fraction (those remaining on the surface) and the lyophilic fraction (those imbibed into the solution) at each surface tension, the distribution of coal particles in relation to their wetting surface tension was determined. This paper shows how such information can be used to delineate the surface characteristics of the particles.

THEORETICAL CONSIDERATIONS

The critical wetting surface tension of a solid is an important parameter that represents the wettability of the solid. It was defined by Zisman as the surface tension of a liquid which forms a zero contact angle on the solid (2). In our earlier research (7,8), we have verified theoretically and experimentally that for practical film flotation, the critical wetting surface tension of coal particles can be taken to be the surface tension of the liquid at which the particles sink into the liquid and that the effect of particle size and density are negligible.

Since we are familiar with the concept of contact angle and because we cannot measure the contact angle of a small particle directly, it is useful to calculate it. The calculation is possible only when γ_c of the particles can be determined by film flotation. By using the Young equation

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV}\cos\theta \qquad (1)$$

and the Neumann/Good equation of state (9):

$$\gamma_{SL} = \frac{(\sqrt{\gamma_{SV}} - \sqrt{\gamma_{LV}})^2}{1 - 0.15\sqrt{\gamma_{SV}\gamma_{LV}}} \qquad (2)$$

we can calculate the contact angle of a particle for a liquid of a given surface tension, γ_{LV}, from the values of γ_c measured in the film flotation experiments. It has been shown that γ_c can be taken as being equivalent to γ_{SV} (9).

Because coal is a mixture of inorganic minerals and organic substances, the surface will appear as a patchwork assembly of carbonaceous material, hydrocarbon, oxygen functional groups and mineral matter. The carbonaceous and hydrocarbon materials contribute to the lyophobic character of coal, whereas the oxygen functional groups and mineral matter contribute to the lyophilic behavior of coal. Therefore, the Cassie-Baxter equation (10) for a composite surface can be used to account for the variation of the contact angle with coal rank (11,12).

To calculate the fraction of lyophobic sites on the surface of coal particles α_{HB} and the fraction of lyophilic sites α_{HL}, we assume that i) the lyophobic sites have a contact angle in water $\theta_{HB} = 105°$ (i.e. paraffin wax) and ii) the lyophilic sites have a contact angle in water $\theta_{HL} = 0°$. Thus,

$$\alpha_{HB} + \alpha_{HL} = 1 \qquad (3)$$

By using Eq. 3 and the Cassie-Baxter equation for a composite surface, we obtain

$$\cos\theta = \alpha_{HB}\cos\theta_{HB} + \alpha_{HL}\cos\theta_{HL} \qquad (4)$$

and can calculate α_{HB} and α_{HL} of coal particles from their contact angles in water.

MATERIALS AND METHODS

Materials used in this study included a number of U.S. coals, Ceylon graphite (99.0% carbon) and sulfur (Nevada). For all materials 100 x 150 μm particles were prepared by grinding the as-received materials in a small ceramic to avoid iron contamination, followed by sizing with sieves. Paraffin wax-coated coal particles were prepared by a simple vapor deposition procedure (11). Oxidation of the coal was carried out thermally in air for 19 hours at 200°C in a mechanical convection oven.

Film flotation experiments (5,6) were conducted by sprinkling the 100 x 150 μm particles onto the surface of the aqueous methanol solutions, with compositions varying from pure water to pure methanol so that the surface tension could be controlled between 22.4 and 72.8 mN/m. For each solution, the fraction of particles remaining at the liquid/vapor interface was determined. All film flotation experiments were carried out at 20°C.

RESULTS AND DISCUSSION

Because of the heterogeneity of coal, the wetting properties of coal particles may change continuously from that of lyophobic organic materials to those of the lyophilic inorganic matter. Figure 1 shows the cumulative distribution of Cambria #78 coal particles as a function of their critical wetting surface tension obtained by film flotation using aqueous methanol solutions. From the results in Fig. 1, the frequency distribution of Cambria #78 coal particles was determined as a function of their critical wetting surface tension and are presented in Fig. 2. These two figures clearly show the heterogeneous nature of coal particles.

From such distributions, four wetting parameters have been defined (5,6). The critical wetting surface tension of the most lyophobic particles in the assembly, γ_c^{min}, is the surface tension of the liquid at which none of the particles remains at the liquid surface. The critical wetting surface tension of the most lyophilic particles in the powder, γ_c^{max}, is the surface tension of the liquid at which all the particles remains at the liquid surface. The mean critical wetting surface tension of all particles, $\bar{\gamma}_c$, can be calculated from the film flotation frequency distribution using the equation:

$$\bar{\gamma}_c = \int \gamma_c \; f(\gamma_c) \; d\gamma_c \qquad (5)$$

where γ_c is the critical surface tension of particles and $f(\gamma_c)$ is the frequency distribution function. $\bar{\gamma}_c$ represents the wettability of the assembly of particles. The standard deviation $\sigma_{\gamma c}$ of the frequency distribution function reflects the heterogeneity of the surface. High $\sigma_{\gamma c}$ values correspond to heterogeneous materials.

Figure 3 shows the frequency distribution of Cambria #78 coal particles as a function of their contact angle in liquids with surface tension of 60.0 and 72.8 mN/m, respectively. The contact angle of the particle for the given liquid surface tension was calculated from their γ_c using Eqs. 1 and 2. The weight percent of particles in different intervals of the contact angle was taken from the distribution presented in Fig. 2. The figure clearly shows that coal particles in an assembly have a wide range of contact angles and that the lower the surface tension of the liquid the smaller the contact angle of the coal particles. This distribution of contact angles serves to illustrate why the coal particles reside at the liquid/vapor surface in film flotation.

The surface composition of coal particles can be related to their wetting properties by calculating the fraction of lyophobic sites on the surface of the particles from their contact angles in water using Eqs. 3 and 4. The frequency distribution of Cambria #78 coal particles as a function of their percentage of lyophobic sites on the surface of the particles is given in Fig. 4. The weight percent of particles in the different intervals shown in Fig. 4 was again taken from Fig. 2. This figure shows that coal particles are covered by varying amounts of lyophobic materials and gives some insight into the extreme heterogeneity of the coal surface.

Table 1. Wetting parameters of as-received, wax-coated and oxidized Cambria #78 coal obtained from film flotation results.

Treatment	$\bar{\gamma}_c$, mN/m	θ, deg.	α_{HB}	$\sigma_{\gamma c}$, mN/m
Wax-coated	25.3	100	0.92	2.60
As-received	43.0	68	0.49	4.53
Oxidized at 200°C for 19 hours	67.0	24	0.07	----

The validity of the film flotation method for characterizing particle surfaces was tested by conducting film flotation tests on wax-coated and oxidized Cambria #78 coal. Figure 5 shows the cumulative distribution of as-received, wax-coated and oxidized Cambria #78 coal particles as a function of their critical wetting surface tension as determined by film flotation. The wetting parameters calculated from the film flotation results are given in Table 1. It can be seen from Fig. 5 and Table 1 that the cumulative distribution of wax-coated coal particles moves to lower wetting surface tensions as compared with that of the as-received coal particles. Also $\bar{\gamma}_c$ of wax-coated coal particles is less than that of as-received coal particles, and the value of θ and α_{HB} for wax-coated coal particles are higher than that of as-received coal particles. This increase in lyophobicity is due to the presence of additional lyophobic sites on the wax-coated coal. On the other hand, the cumulative distribution curve of oxidized coal particles moves to higher wetting surface tensions and its $\bar{\gamma}_c$ value is higher than that of as-received coal particles. The value of θ and α_{HB} oxidized coal particles are smaller than that of as-received coal particles, indicating, as expected, that coal particles are more lyophilic when they are oxidized due to the destruction of lyophobic sites by the oxidation process. These findings serve to confirm our film flotation approach.

To further verify our new approach, the mean contact angle of a particle assemblage was compared with the values reported for direct measurements on the flat surface of a bulk sample. Since a flat surface of a bulk sample can be considered to be a composite of small particles with different contact angles, the contact angles

Table 2. The contact angles, θ, of sulfur, graphite and coals in water calculated from film flotation results, and measured by captive-bubble (CB) and sessile-drop (SD) methods.

Mineral	Film Flotation θ, degrees	Contact Angle Measurement θ, deg.	Method	Ref.
Sulfur	86	87	SD	(13)
Graphite	71	77	CB	(14)
Braztah Coal	87	90	SD	(15)
Somerset Coal	74	56	SD	(15)
Cambria #33 Coal	62	57	CB	(14)
		85	CB	(4)
		91	SD	(4)
Geneva Coal	81	72	SD	(15)
		86	SD	(15)
		64	CB	(14)

obtained from both methods should agree with each other if our approach is correct and if the polishing procedures used in preparing the flat surface do not change its wetting properties significantly. The contact angle of sulfur, graphite and various coals in water calculated from film flotation results are presented in Table 2. This table also shows the contact angle measured by captive-bubble and sessile-drop methods on a flat surface of the same samples in our laboratory. From this table it is seen that the two sets of values are in quite good agreement with each other, especially for the more homogeneous minerals. This further supports the model for the estimation of the contact angle of particles from their critical wetting surface tension.

SUMMARY AND CONCLUSIONS

The distribution of the critical wetting surface tension of an assemblage of particles was determined using the film flotation method. A model has been developed to estimate the contact angle of coal particles from the critical wetting surface tension distribution and to estimate the fraction of lyophobic sites on the surface of these particles from this calculated value. The estimated mean contact angle of particles is in good agreement with measured values on flat surfaces. This model provides insight into the heterogeneous nature of coal particles.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the U. S. Department of Energy, Pittsburgh Energy Technology Center, Grant No. DE-FG22-86PC90507

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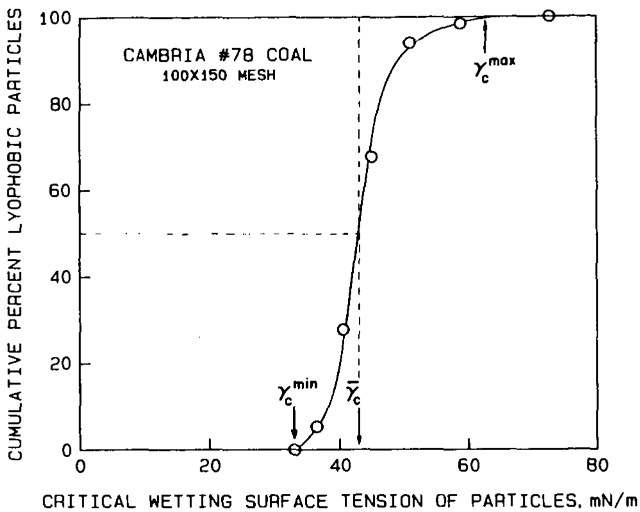

Fig. 1- The cumulative distribution of Cambria #78 coal particles as a function of their critical wetting surface tension obtained from film flotation with aqueous methanol solutions.

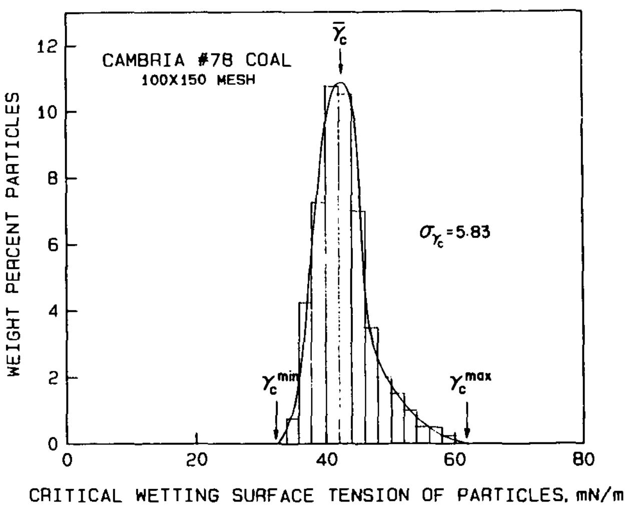

Fig. 2- Frequency distribution of Cambria #78 coal particles as a function of their critical wetting surface tension determined from film flotation with aqueous methanol solutions.

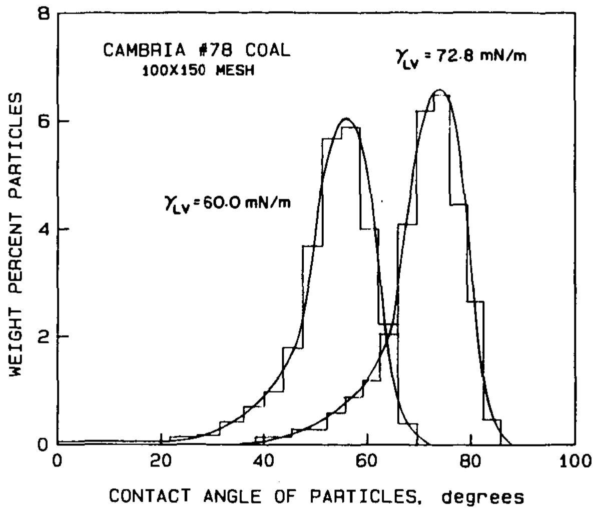

Fig. 3- Frequency distribution of Cambria #78 coal particles as a function of their contact angle in the liquid with surface tension of 60.0 and 72.8 mN/m, respectively.

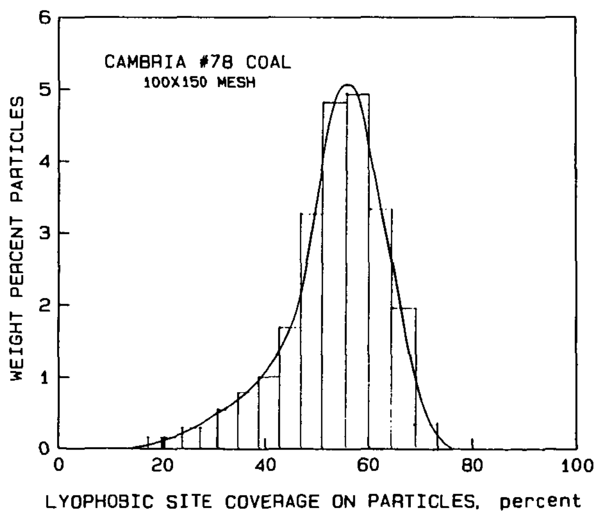

Fig. 4- Frequency distribution of Cambria #78 coal particles as a function of lyophobic sites on the surface of the particles.

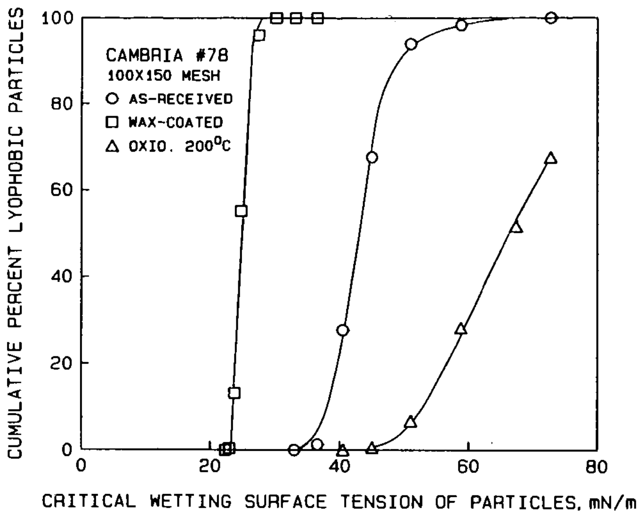

Fig. 5- Cumulative distribution of as-received, wax-coated, and oxidized (200°C, for 19 hours) Cambria #78 coal as a function of their critical wetting surface tension determined from film flotation with aqueous methanol solutions.